

COPROCESSING OF POLYMERIC WASTE WITH COAL: REACTION OF POLYETHYLENE AND COAL MODEL COMPOUNDS

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ABSTRACT

Environmental and economical concerns over diminishing landfill space and the growing abundance of mixed plastic waste mandate development of viable strategies for recovering high-valued resources from waste polymers. Co-processing of waste polymer mixtures with coal allows for the simultaneous conversion of coal and plastics into high-valued fuels. However, there is limited information about the underlying reaction pathways, kinetics, and mechanisms controlling coal liquefaction in the presence of polymeric materials.

A series of model compound experiments has been conducted, providing a starting point for unraveling the complex, underlying chemistry. Neat pyrolysis studies of model compounds of polyethylene and coal were conducted in batch reactors. Tetradecane ($C_{14}H_{30}$) was used as a polyethylene mimic, and 4-(naphthylmethyl)biphenyl was used as a coal model compound. Reaction temperatures were 420 and 500°C, and batch reaction times ranged from 5-150 minutes. Detailed product analysis using gas chromatography and mass spectrometry enabled the reactant conversion and product selectivities to be determined. Reaction of single components and binary mixtures allowed the kinetic coupling between feedstocks to be examined.

INTRODUCTION

Recently, concerns over the inadequacy of current treatment and disposal methods for mixed plastic wastes have driven the exploration of new strategies for viable plastics resource recovery. The emphasis of the recovery is to obtain high-valued, useful products from the waste polymers. Post-consumer waste plastics are a major contributor to the municipal solid waste (MSW) stream, constituting approximately 11% by weight and 21% by volume of waste in landfills¹. Over 40% of the landfills in the United States were closed in the past decade, and it is estimated that over half of the remaining ones will be full by the end of the century². This poses a significant dilemma since there appears to be no immediate decrease in the usage of plastic products; in fact, due to their versatility, the usage will most likely increase.

The current motivation for the recovery of plastics is due to government mandates, rather than to industrial initiatives. Some states, such as California, Oregon, and Wisconsin, have passed laws which specify that plastic bottles must be manufactured from a minimum of 25% recycled plastics. Germany has dictated that over 80% of all plastic packaging must be recycled by methods other than combustion by 1996³⁻⁵. Conventional plastics recycling technologies encounter a number of difficulties which range from costly separation to removal of impurities and contaminants. A consequence of these problems is that products manufactured from recycled polymers are of lower quality and higher cost (approximately 10% higher for high-density polyethylene (HDPE)) than those from the corresponding virgin polymer⁴. As a result, in the United States, only about 4% of 30 million tons of total plastics produced each year is recycled⁶.

Coprocessing of polymeric waste with other materials may provide potential solutions to the deficiencies of current resource recovery processes, including unfavorable process economics. By incorporating polymeric waste as a minor feed into an existing process, variations in plastic supply and composition could be mediated and as a result, allow for continuous operation. One option for coprocessing is to react polymeric waste with coal under direct liquefaction conditions^{2,7,8}. Coprocessing of polymeric waste with coal provides for simultaneous conversion of both feedstocks into high-valued fuels and chemicals.

EXPERIMENTAL

In order to obtain information about underlying reaction pathways, kinetics, and mechanisms without the complicating effects of the macrostructure, experiments were performed using model compounds for both coal and polyethylene, a voluminous component of mixed plastic waste. To mimic the structure of coal, 4-(naphthylmethyl)biphenyl (NBBM) was used. NBBM contains both condensed and isolated aromatic species connected by short alkyl chains. An added feature is that it contains five different aromatic-aliphatic or aliphatic-aliphatic carbon-carbon bonds. Successful predictions of the relevant primary products for real systems using NBBM confirmed the adequacy of this model compound, and thus, it will be employed in this study⁹⁻¹². The structure of NBBM is depicted in Figure 1. Although numerous hydrocarbons may serve as appropriate model compounds for high density and low density polyethylene, tetradecane, $C_{14}H_{30}$, was chosen as an appropriate compromise in reactant size.

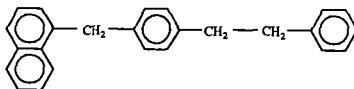


Figure 1: Structure of coal model compound 4-(naphthylmethyl)biphenyl.

Batch pyrolyses were carried out in an isothermal ($\pm 1^\circ\text{C}$) fluidized sand bath. The experiments were conducted in 2 ml glass cryovials charged with ca. 20 mg of reactant for the neat reactions. Equimolar ratios of tetradecane/NBBM were used for the binary experiments, with loadings based on ca. 10 mg of NBBM. After filling, the ampoules were purged with argon, and then sealed using an oxygen/propane flame. Pyrolysis was conducted at both 420 and 500°C, and reaction times ranged from 5-150 minutes. Upon completion of the reaction period, the ampoules were removed from the sand bath and permitted to cool at room temperature. The experiments were replicated a minimum of two times, and conversions and selectivities were reproducible with an error of less than 1%.

Soluble reaction products were extracted from the ampoules using 5 ml of methylene chloride, and an external standard (biphenyl) was added. Product identification and quantification, which enabled reactant conversions and product selectivities to be determined, was achieved using an HP 6890 GC/MS and HP 5890 GC equipped with a flame ionization detector, respectively, each employing a Hewlett Packard 30 m crosslinked 5% Ph Me Silicone capillary column.

RESULTS AND DISCUSSION

The reactant conversions for pyrolysis of tetradecane and NBBM at 500°C were very high, as almost complete conversion was achieved at a reaction time of 10 minutes for all the systems studied. As evidenced by the product spectra and the temporal variations of the major products, secondary and tertiary reactions occurred, making it difficult to deconvolute reaction pathways. Therefore, the reaction temperature was lowered to 420°C, a value still within the range of relevant liquefaction conditions, to achieve lower conversions and isolate primary decomposition pathways. It was noted from the data at 500°C, however, that the conversion of tetradecane was enhanced slightly in the presence of NBBM as compared to the neat reaction.

Reactions carried out at 420°C facilitated identification of the underlying reaction pathways and kinetics. As illustrated in Figure 2, the conversion was significantly lower at a given reaction time as compared to that observed at 500°C. For example, only 37 % of the tetradecane was converted after 150 minutes of reaction time.

The major products observed from the pyrolysis of tetradecane were α -olefins, with minor selectivity to n-alkanes. The highest selectivity, 0.13, was obtained for 1-heptene, and α -olefins with carbon numbers of 6 to 11 were also observed in significant quantities. As reaction time increased, the selectivity to α -olefins decreased, while that of n-alkanes slightly increased, as observed in Figure 3. This behavior can be explained by noting that hydrogenation of olefins and continued thermal cracking can occur as reaction time increases.

The product distribution was rationalized in terms of the typical free radical Rice-Herzfeld and Rice-Kossiakoff mechanisms¹³⁻¹⁶. The mechanism is initiated by carbon-carbon bond fission along the main chain to form two primary radicals. These primary radicals form secondary radicals through hydrogen abstraction from a secondary carbon or an intramolecular hydrogen rearrangement. These secondary radicals then undergo β -scission to form α -olefins and primary radicals. Termination occurs by recombination of radicals.

Two of the major products from pyrolysis of NBBM, which are formed by carbon-carbon bond fission and subsequent hydrogen abstraction, were toluene and 1-methyl-4-(naphthylmethyl) benzene, each observed with a selectivity of greater than 0.28 at all reaction times studied. The other major product was 1-(2-phenylethenyl)-4-(naphthylmethyl) benzene, with an initial selectivity of approximately 0.35 which decreased linearly with reaction time to 0.11 at 150 minutes. Minor selectivities were observed for a number of products from NBBM pyrolysis. Methyl bibenzyl and 1-(4-(4-methyl)phenylmethyl)benzyl naphthalene were observed with initial selectivities of 0.055 and 0.070, respectively. Other minor products included 1,4-(binaphthylmethyl) benzene, phenyl methyl naphthalene, naphthalene, methyl naphthalene, 1-(phenylmethyl)-4-(naphthylmethyl) benzene, 1-methyl-4-(2-phenylethenyl) benzene and p-xylene.

Mechanistic interpretation using the ideas put forth by Walter et al. (1994) successfully accounted for the observed product spectra. The products anticipated from scission of the five main bonds of NBBM, labeled A-E, and subsequent hydrogen abstraction and β -scission, are depicted in Figure 4. The formation of high yields of toluene and 1-methyl-4-(naphthylmethyl) benzene is consistent with the proposed mechanism involving bond D fission. This is the weakest bond in the molecule, since the radicals which are formed can be stabilized by the adjacent benzyl substituents. Similarly, the C₁ linkage in NBBM possesses the most easily abstractable hydrogens. Once a secondary radical is formed, it can undergo β -scission to form 1-(2-phenylethenyl)-4-(naphthylmethyl) benzene. This compound could then undergo degradation reactions similar to those observed for NBBM, leading to a reduction in selectivity as reaction time increases.

A comparison of the selectivities of products associated with cleavage of bond A as a function of conversion is shown in Figure 5. If these products were solely formed by bond A scission, it would be expected that the selectivities would be equal for naphthalene and the sum of methyl bibenzyl and its corresponding derivatives. This is clearly not the case. Therefore, another reaction pathway for the formation of these products must exist. Upon examination of other bond scission pairs, a discrepancy between bond C products, phenyl methyl naphthalene, which was observed, and ethylbenzene, which was not, was noted. Also, as stated, other products which can not be explained by one of the five bond scissions were observed, which leads to investigation of secondary pathways. These observations are consistent with a free radical ipso-substitution scheme for the formation of the various products as proposed by Walter et al. (1994). For example, attack by a benzyl radical of the NBBM molecule at the 1-naphthyl position would afford phenyl methyl naphthalene. This scheme would involve the formation of a mole of naphthalene and phenyl methyl naphthalene for every mole formed of methyl bibenzyl and its derivatives. This

comparison is presented in the plot of Figure 6. Likewise, various radical attack at bond C can explain the appearance of 1-(4-(4-methylphenylmethyl)benzyl) naphthalene, 1,4-(binaphthylmethyl) benzene, and 1-(phenylmethyl)-4-(naphthylmethyl) benzene. Overall, the main reaction families for NBBM pyrolysis are therefore bond thermolysis, hydrogen abstraction, radical ipso-substitution, β -scission, and radical recombination¹².

Reactions of binary mixtures of tetradecane and NBBM revealed interactions between the reactants and synergistic effects. As observed in Figure 2, tetradecane conversion was increased in the presence of NBBM, which can be rationalized in terms of kinetic coupling¹⁷. The internal carbon-carbon bonds of tetradecane have a higher bond dissociation energy (90 kcal mol⁻¹) than that of bond D in NBBM (60 kcal mol⁻¹)¹⁸. This has the potential to increase the quantity of radicals in the system with respect to the neat tetradecane experiments at a particular reaction time. The NBBM-derived radicals can easily abstract hydrogen from the secondary carbons of tetradecane, forming a tetradecane-derived radical and converting a tetradecane molecule, enhancing its conversion. Once formed, these tetradecane-derived radicals undergo their own decomposition reactions as observed for neat pyrolysis, and similar product yields are observed.

The interactions between NBBM and tetradecane can be further supported by examining the products derived from NBBM. Since abstraction of hydrogen from tetradecane is facile and has a high reaction path degeneracy of 24, NBBM radicals are capped and stabilized through this abstraction step before undergoing secondary reactions. This effect on the overall product yields can be discerned from Figure 7. The radicals formed from bond D thermolysis abstract hydrogen with higher selectivity and afford higher yields of toluene. Correspondingly, the selectivity to the radical ipso-substitution pathway and formation of phenyl methyl naphthalene is diminished. Therefore, it can be seen that during low pressure pyrolysis, favorable interactions between the two reactants exist. The effective tetradecane conversion is increased, and primary product selectivities are enhanced.

CONCLUSIONS

Recent investigations have demonstrated the feasibility coprocessing of coal with polymers. In this study, feedstock interactions were observed using model compound mimics of both coal and polyethylene. In binary mixtures, the conversion of tetradecane increased while the selectivity to primary products of NBBM pyrolysis was enhanced. These observations were attributed to the stabilization of NBBM-derived radicals through hydrogen abstraction from tetradecane which in turn, increases the rate of tetradecane conversion. In order to optimize the interaction between reactants, further experimental and theoretical studies will be conducted at high pressures and in the presence of catalysts in order to delineate the underlying kinetics, pathways, and mechanism controlling coal/polymer coprocessing.

ACKNOWLEDGMENTS

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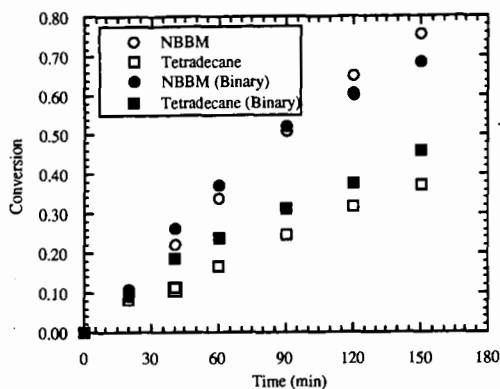


Figure 2: Conversion of tetradecane and NBBM, neat and in binary mixtures, at 420 °C.

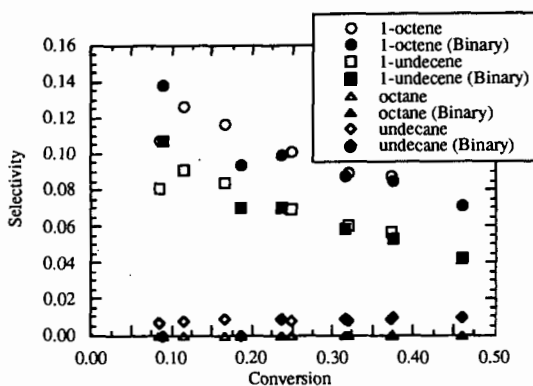


Figure 3: Comparison of alkane/alkene selectivities during neat and binary mixture reactions.

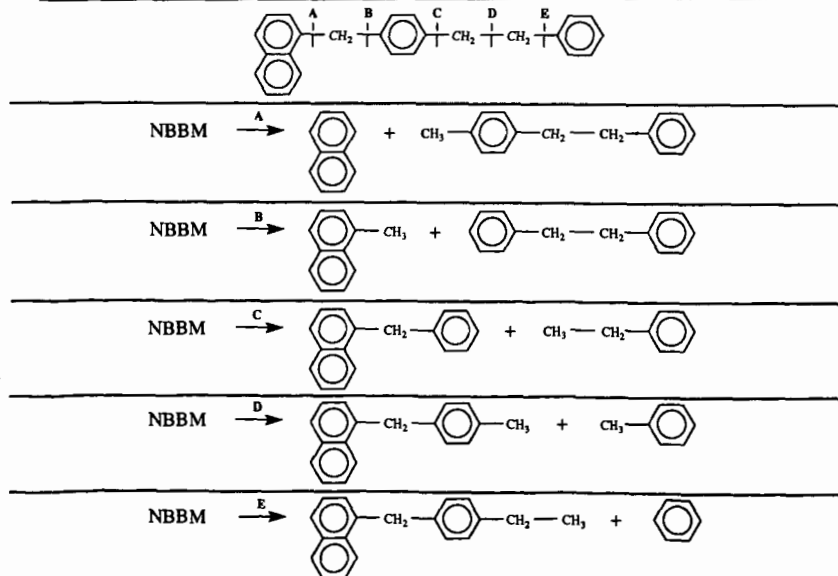


Figure 4: Bond assignment and corresponding products of NBBM pyrolysis, allowing for only bond fission, hydrogen abstraction, and β -scission.

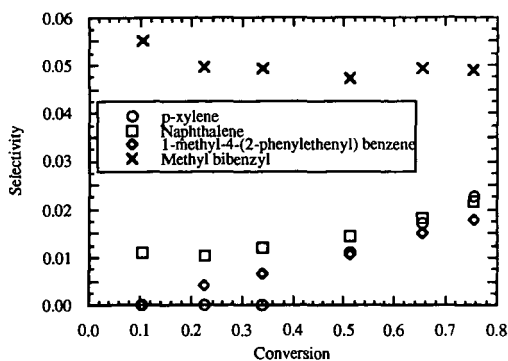


Figure 5: Comparison of selectivities of products associated with cleavage of bond A as a function of conversion.

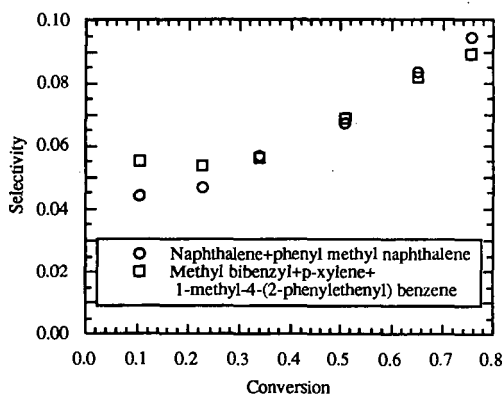


Figure 6: Comparison of products from free radical ipso-substitution reaction which accounts for cleavage of bond A.

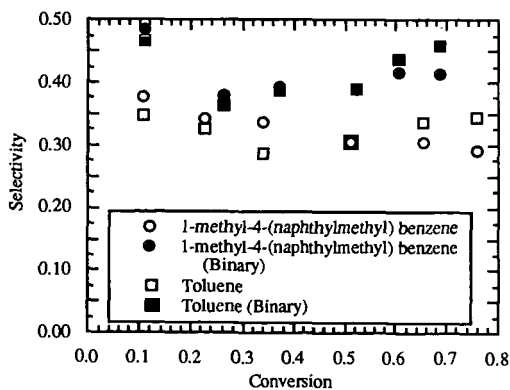


Figure 7: Comparison of products from bond D cleavage during neat NBBM and binary mixture reactions.